UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 4
ATLANTA FEDERAL CENTER
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DEC 3 0 2003

4APT-ATMB

John Lyons, Director
Division of Air Quality
Department for Environmental Protection
Natural Resources and Environmental
Protection Cabinet
803 Schenkel Lane
Frankfort, Kentucky 40601

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To Kent Kriesbauer	From David McNeal
Dept./Agency	Phone # 404-562-9102
Fax # 610-458-6186	Fax #

NSN 7540-01-317-7368 5099-101 GENERAL SERVICES ADMINISTRATION

Dear Mr. Lyons:

The purpose for this letter is to provide you with a determination regarding an alternative monitoring proposal that Air Products and Chemicals, Incorporated submitted for refinery fuel gas streams that are burned in a reformer furnace at the company's Catlettsburg, Kentucky hydrogen plant. These fuel gas streams are subject to a sulfur dioxide (SO_2) emission limit under 40 CFR Part 60, Subpart J (Standards of Performance for Petroleum Refineries), and Air Products has proposed an alternative to the SO_2 continuous monitoring requirements in Subpart J. Based upon our review, the proposed alternative monitoring approach which relies on using detector tubes to determine the hydrogen sulfide (H_2S) concentration of the raw materials for reformer is acceptable. Details regarding the company's proposal and the basis for our conclusions are provided in the remainder of this letter.

The fuels burned in the hydrogen reformer at Air Products are natural gas, syngas, and pressure swing adsorption (PSA) purge gas. Both the syngas and PSA purge gas meet the definition of fuel gas promulgated at 40 CFR §60.101 (i.e., any gas which is generated at a petroleum refinery and which is combusted), and 40 CFR §60.104(a)(1) limits the H_2S content of gases burned in fuel gas combustion devices to 230 milligrams per dry standard cubic meter. Owners/operators subject to this H_2S limit are required to install a continuous emission monitoring system (CEMS) to measure either the SO_2 emission rate from fuel gas combustion devices or the H_2S concentration in the fuel gas streams burned. These monitoring requirements are promulgated at 40 CFR §60.105(a), and as an alternative to installation of either an SO2 or an H_2S CEMS, Air Products proposed a monitoring approach previously approved by the U.S. Environmental Protection Agency (EPA) Region 5 for a Koch Petroleum Group refinery located in Pine Bend, Minnesota.

Under the proposed alternative monitoring plan, "length-of-stain" detector tubes would be used to measure the H_2S concentration of the feed stream (natural gas and recycled hydrogen) exiting the first of two hydrogenator/desulfurizer beds located upstream of the hydrogen reformer furnace. The proposed alternative monitoring plan includes the following steps:

1. Random H_2S detector tube samples shall be collected twice a week for six months. If the average plus three standard deviations for this data set is less than 81 parts per million (ppm), proceed to step 2. The 81 ppm threshold used when deciding to proceed to the next step corresponds to 50 percent of the applicable H_2S limit in Subpart J.

2. Random H_2S detector tube samples shall be collected once a quarter for six quarters with a minimum duration of one month between samples. If the average plus three standard deviations for this data set is less than 81 ppm, proceed to step 3.

3. Random H_2S detector tube samples shall be collected twice a year for two years. These samples shall be collected in the first and third quarters of the year with a minimum of three months between samples. If the average plus three standard deviations for this data set is less than 81 ppm, proceed to step 4.

4. Random H_2S detector tube samples shall be collected on a semi-annual basis with a minimum of three months between samples.

5. If any detector tube checks indicate that the H_2S concentration at the outlet of the first hydrogenator/desulfurizer module exceeds 81 ppm, additional detector tube samples shall be collected on a daily basis for seven days. If the average plus three standard deviations for this data set is less than 81 ppm, monitoring shall resume in accordance with the alternative schedule at the current step. If the average plus three standard deviations for this data set is 81 ppm or higher, proceed to step 6.

6. By the end of the next business day following the last sample for a data set indicating that the average plus three standard deviations equals or exceeds 81 ppm, the Agency shall be notified of the results. Additional detector tube samples shall be collected on a daily basis for a two-week period for a total of 14 samples. Following the completion of the two week period, detector tube sampling shall be conducted once per week until the Agency either approves a revised sampling schedule or withdraws approval for the use of an alternative monitoring plan.

Because of the way the company's Catlettsburg hydrogen plant is designed, the H_2S concentration in the syngas and the PSA purge gas burned as fuel in the reformer furnace should always be well below the applicable standard. Natural gas, recycled hydrogen product, and steam are the raw materials for the hydrogen plant, and the H_2S concentration in all three of these feed streams is low. The gas stream produced when these feed streams react in the presence of catalyst in the reformer is called syngas, and this stream contains the desired product (hydrogen), carbon monoxide (CO), carbon dioxide (CO_2), methane, and water. The syngas leaving the reformer is sent to a high temperature shift (HTS) reactor where most of the CO present in the gas stream is converted to CO_2, and the HTS effluent is sent to the pressure swing absorption unit where the hydrogen product is purified. The PSA purge gas routed back to the reformer and

burned as fuel consists of impurities (primarily CO, CO2, hydrogen, and methane) removed from the hydrogen product.

PSA purge gas is the primary fuel for the reformer furnace during normal operation, but Air Products has the ability to route syngas back to the furnace and burn it as fuel if the pressure swing absorption unit malfunctions and must be taken off line. Although both syngas and PSA purge gas meet the definition of refinery fuel gas, the sulfur content of both gas streams should be extremely low since the natural gas used as feedstock for the hydrogen plant has a low sulfur content and goes through a desulfurization step before it is sent to the reformer furnace. In addition, Air Products has a significant financial incentive to keep the H_2S content of the reformer feed streams as low as possible since sulfur present in the these gas streams will poison the catalyst in the hydrogen reformer. Due to the inherently low sulfur content of the raw materials for the hydrogen reformer and process considerations that require that the H_2S content of the raw materials be kept low, the monitoring approach that Air Products proposed as an alternative to installation of either an SO_2 or H_2S CEMS is acceptable to EPA Region 4.

If you have any questions about the determination provided in this letter, please contact Mr. David McNeal of the EPA Region 4 staff at (404) 562-9102.

Sincerely,

Douglas Neeley for

Beverly H. Banister
Director
Air, Pesticides and Toxics
Management Division

cc: Donald Newell
Carla Mings

bcc: Beverly Spagg
Dick Dubose